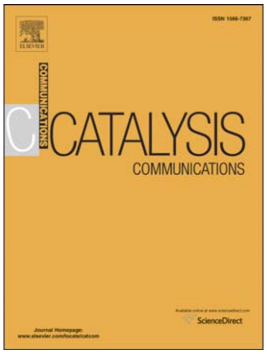

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Selective Oxidation of DDT by Dioxygen on the Dioxo-Mo(VI) Complex Anchored on a TiO_2 Under UV-irradiation

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Abstract

Oxidation of DDT (1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane) by the dioxo-Mo(VI) complex (dioxo-molybdenum(VI)-dichloro[4,4′-dicarboxylato-2,2′-bipyridine]), anchored on a TiO_2, in the presence of dioxygen under UV-irradiation (λ= 253.7nm) in acetonitrile suspension has been examined. The reaction has catalytic character. Conversion of DDT (35% for 32 h reaction) to dicofol (2,2,2-trichloro-1,1-*bis*-(4-chlorophenyl)ethanol, 21%) and a great number of other chlorinated and non-chlorinated products of the oxidative/reductive decomposition proceeds by the primary reaction of oxo-atom transfer from dioxo-Mo(VI) complex to bibenzylic– carbon atom of DDT. The catalytic cycle is performed via the re-oxidation of the reduced Mo(IV) into Mo(VI) by dioxygen in the "dark" reaction.

Keywords: catalytic oxidation; dioxo-Mo(VI)-complex anchored on a TiO_2; DDT; dicofol

1. Introduction

Oxo-Mo complexes, bearing specific organic ligands, possess a capacity of the selective oxidation of aryl alkanes, phosphines, olefins and alcohols [1-5]. It has been established that the primary chemical process begins from the transfer of oxo-atom of these complexes to substrates [4, 5]. Oxidizing agents, such as O_2, H_2O_2, O_3, DMSO and others, in certain conditions, are able to re-oxidize the reduced metal atom, providing the catalytic cycle.

The catalytic activity increases, when these complexes are supported on the solid substances or anchored on the solid matrix with covalent chemical bonds [6-9]. One of the best examples of this is dioxo-Mo(VI)-dichloro[4,4′-dicarboxylato-2,2′-bipyridine], anchored on TiO_2 (P25) (Complex 1),

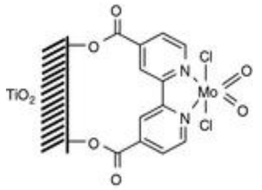


Fig. 1. Complex 1. Dioxo-molybdenum(VI)-dichloro[4,4′-dicarboxylato-2,2′-bipyridine], anchored on TiO_2.

the activity of which as a catalyst has been tested in oxidation of trimethylphosphine, ethylbenzene, tetraline, diphenylmethan with O_2 [7-10], as well as, in oxidation of chlorinated hydrocarbons (1-chloro-4-ethylbenzene and 2,2-*bis*-(p-chloropheny)methane) [11, 12].

The selective oxidation of halogenated hydrocarbons are of interest in various areas, such as chemical industry, green chemistry, organic syntheses [13]. Particularly DDT(1,1,1-trichloro-2,2-*bis*-(4-chlorophenyl)ethane), mainly known as a pesticide and persistent pollutant, also is a primary reactant for the production of dicofol (2,2,2-trichloro-1,1-*bis*-(4-chlorophenyl)ethanol). In chemical industry the oxidation of DDT, directed to the production of dicofol is performed as a multistep process, including: elimination of HCl from DDT, giving DDE (1,1-*bis*-(4-chlorophenyl)-2,2-dichloroethene); chlorination of DDE to tetramer (dichlorodiphenyltetrachloroethane); hydrolysis of tetramer to dicofol, using para-toluene sulfuric acid [14].

The aim of this work is to evaluate the feasibility of a direct oxidation of DDT with dioxygen under "mild" conditions, by the application of Complex (1), under UV-irradiation, in order to achieve the selective formation of oxygenated products, other than its total TiO_2 induced photodegradation obtained in water.

2. Experimental

2.1 Experimental setup and materials

The specially designed experimental setup consisting of photochemical reactor (quartz, 30 mL) with a magnetic stirrer and optical junction for UV-irradiation (λ= 253.7nm), high pressure Hg-lamp (DRT- 230, Russia), as well as the procedure of measurements were described in [11].

DDT, dicofol, DDE, and nearly all other chemicals (Sigma-Aldrich) were used as received. Acetonitrile (Merck, Germany) was distillated by an ordinary procedure, in argon atmosphere.

The Complex (1), was synthesized by the method described in [10, 15] and characterized mainly by ^{13}C CAP NMR method [10,16]. The amount of the anchored complex on the TiO_2, determined by TGA analysis (TG- 2950 Hi Re), was about 1,6 x10^{-4} mol per gram.

2.2. Procedures

Reaction mixture was a suspension of DDT (5,73 mg =1.6 x 10^{-5} mol) in 10 mL acetonitrile, containing 10 mg of the Complex (1). Each experimental cycle was consisted of two consecutive periods: in the first period, the reaction mixture while stirring was exposed under UV-irradiation, in argon atmosphere and in the absence of dioxygen during 6-7 h, then, in the second period, the reaction was carried out without UV-irradiation and in the presence of dioxygen ("dark" period, 2-2,5 h). Before the beginning of a new experimental cycle, dioxygen was thoroughly removed from the reaction mixture during 1.5-2 h. All experiments were carried out at the room temperature.

Identification and analysis of the products were carried out by gas-liquid chromatography (electron capture detector), using column with SE-30 sorbent, the control analysis were carried out by chrommass-spectrometer DANI Master DC TOF, using capillary column (30 m) coated by DB-ALC2. Analysis of Cl-ions, were performed by chemical methods (argentometric way by the Mohr method).

3 . Results and Discussion

Experimental results of the consumption of DDT in 5 consecutive cycles are presented in Fig. 2. The horizontal sections on the curve (a) correspond to the second periods, the aim of which is re-oxidation of Mo(IV), formed in the first period, into Mo(VI) with dioxygen. The curve (b) corresponds to the photochemical oxidation of DDT on the surface of "pure" TiO_2 (without anchored complex on TiO_2), in the presence of dioxygen. Note, the amount of the "pure" TiO_2 in reaction mixture was twice that of experiments with the Complex (1). The simple comparison of two curves indicates a significant increase of the consumption of DDT in the presence of the anchored complex.

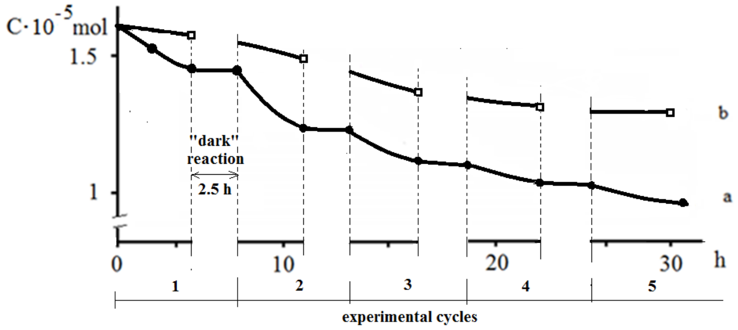


Fig.2. Time profiles of the consumption of DDT(C x10^{-5} mol) under UV- irradiation: (a) - in the presence of the anchored Complex (1); (b) - in the presence of the "pure" TiO_2 (in amounts 2 times more than Complex (1)) and O_2.

The turnover number, a molar ratio Δ[DDT] / [anchored complex], at the last experimental cycle is about 3,7 (corresponding to 35% conversion in 32 h reaction) (Table 1.). Under the same conditions, but in the absence of the anchored complex, the photooxidation of DDT on "pure" TiO_2 is a relatively slow process (13% conversion of DDT for the same time period, Fig. 2. b). The above facts indicate the catalytic character of the overall process in the presence of the anchored Complex (1).

Table 1. Experimental data of the dependence of the turnover number Δ[DDT]/[anchored complex] and yield of dicofol on the number of experimental cycle (the reaction time (h) is given in parentheses).

Number of the experimental cycle	1	2	3	4	5
Turnover number	0.63 (5)	2.13(11)	2.58(17)	3.38(23)	3.68(32)
Yield of dicofol (%)	9.5	13,5	15,4	18,2	21

The reaction products include large spectra of the chlorinated and non-chlorinated organic compounds (C_2-C_{14}), as well as the products of the complete destruction, such as CO_2, H_2O, HCl. Among them, taking into account the results of the chromatographic analyses and overall amount of the analyzed Cl^- ions, the sum of a dozen products of the complete dechlorination was estimated as about 53-57%. Correspondingly, other products (43-47%) are non-dechlorinated and partially dechlorinated compounds. The main product of the reaction is dicofol (21 %), playing also the role of an intermediate for a number of other chlorinated and non-chlorinated products. Note, under the same conditions, but in the absence of the anchored complex ("pure" TiO_2), the formation of dicofol was very slow, and the reaction gives a more complex mixture of other oxidative/reductive decomposition products, including the products of the complete degradation in small amounts.

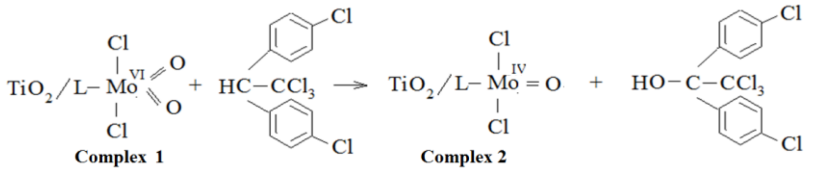
The second main product of the reaction is DDE (9%). All other products of the oxidative decomposition of DDT, nearly are the same as observed in the photochemical decomposition of dicofol on TiO_2 in the presence of oxygen [17]. Among them 4,4'-dichlorobenzophenone (3-4%), prevails over others in our experiments. However, the composition of products in the presence of the anchored complex on a TiO_2 has some obvious differences, than referred [17]. The reaction mixture contains also products of the reductive decomposition, such as DDD (1,1-dichloro-2,2-*bis*-(p-chlorophenyl)ethane), DDM (2,2-*bis*-(p-chloropheny)methane), diphenylmethane, and others, for a total 13-14%. One should note the similarity in the composition of the reaction products between the enzymatic oxidation of DDT and the results of the present work. For example: in biodegradation of DDT by so called White Rot Fungus

Phanerochaete chrysosporium, the formation of the oxidative (2,2-dichloro-1,1-bis(4-chlorophenyl)ethanol and 4,4'-dichlorobenzophenone), as well as reductive degradation (DDD, DDM) were identified [18].

The formation of dicofol can be rationalized in terms of the oxygen atom transfer process [4,5,9-12]. The suggested catalytic cycle is depicted in Scheme 1. A primary reaction between DDT and Complex (1) gives dicofol and a reduced Mo(IV)-oxo Complex (2). In the second period, in the "dark", the Complex (2) is re-oxidized by O_2 to give Mo(VI)-oxo-peroxo Complex (3). The first period, of the second cycle under argon and UV-irradiation allows the transfer of two oxygen atoms to DDT, one peroxo and one oxo, to give two molecule of dicofol, regenerating Mo(IV)-oxo Complex (2) (reaction 3 and 1).

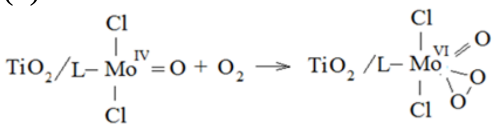
Scheme 1

(1)



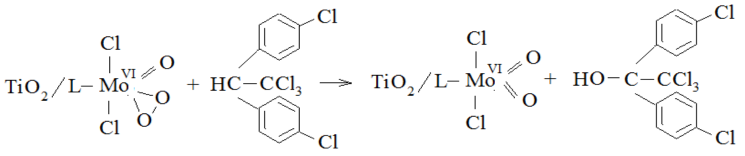
where L is 4,4′-dicarboxylato-2,2′-bipyridine

(2)



Complex 3

(3)



An increase of the turnover number, as well as the yields of dicofol in the second and further cycles (Table 1), probably, are related to the reactions of Complex 3, enable to transfer twice more oxygen atoms to DDT, than Complex 1.

As an indirect evidence of the reactions (1-3) may be served a number of examples of the analogous oxidation processes, of the chlorinated (1-chloro-4-ethylbenzene, 4,4'-dichlorodiphenylmethane) [11,12] and non-chlorinated hydrocarbons (ethylbezene, diphenylmethane) [9, 10], in same or similar conditions. In all mentioned cases, the oxo-atom transfer to the benzylic or bibenzylic carbon atom is considered as the main primary reaction, resulting the formation of the corresponding alcoholic compound.

4. Conclusions

The observed reaction of the direct photocatalytic oxidation of DDT with dioxygen opens an attractive opportunity for the elaboration of an alternative method of the selective oxidation of DDT under "mild" conditions, using the anchored complexes, containing the transition metal oxo-atoms, on a TiO_2, under UV-irradiation or sunlight. Apparently, it may be assumed a complex mechanism of the oxidation of DDT with O_2 in the presence of the Complex (1), under UV-irradiation, including a combination of the primary transfer of oxo- or peroxo-atom of oxygen from Mo(VI) to the substrate accompanied with a number of further decomposition reactions.

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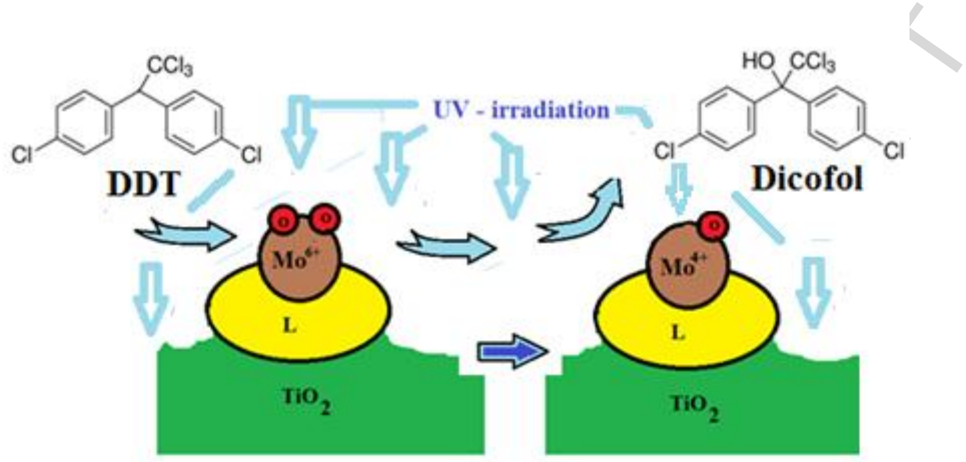
GRAPHICAL ABSTRACT



Reaction of O=Mo^{VI}(O)(Cl$_2$)|[L]/TiO$_2$ with DDT, L is 4,4′-dicarboxylato-2,2′-bipyridine.

Highlights

- $Mo^{VI}O_2Cl_2L/TiO_2$ complex is a catalyst for photooxidation of DDT by O_2.
- The main product is dicofol (21%) and the conversion is 35% for 32 hours reaction.
- The oxo-atom transfer of Mo^{VI} to the bibenzylic-carbon of DDT is primary reaction.
- Catalytic cycle includes re-oxidation of Mo^{IV} to Mo^{VI} by O_2 in the “dark” reaction.